

# A formulation for dissolution in inhomogeneous temperature field

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## Abstract

*We propose equations governing the dissolution in inhomogeneous temperature field in terms of the variational principle. The derived equations clarify that the interface energy between solute and solvent has a significant effect on the process of the dissolution. The interface energy restrains the dissolution, and the moving interface involves the heat of dissolution.*

## Introduction

Dissolution is an important process and frequently discussed in industry as well as in science. For example, the dissolution of supercritical CO<sub>2</sub> in interstitial water is one of the most crucial research topics in CO<sub>2</sub> capture and storage (CCS), which stores the CO<sub>2</sub> into the deep underground in a geological rock formation. The CO<sub>2</sub> can be trapped in the micro-pore space as droplets surrounded by water. At this small scale, the contribution of the interface energy to the total energy is consequential, and thus comes into play. Various phase field models based on free energies are often used to study the dynamics on the assumption of constant temperature and no heat transfer[1, 2]. There can be phenomena involved in the inhomogeneous temperature and the heat transfer. The diffusion flux can be induced by a temperature gradient, which is known as the Soret effect or thermal diffusion[3]. The heat transfer during dissolution across the interface is also considered important for the dynamics of the gas CO<sub>2</sub> at near the critical point because of its very large thermal conductivity[4]. In previous works, heuristic methods have been proposed to combine the thermodynamics with those phase field models above. In this study, we propose a completely different method based on the variational principle to derive the gov-

erning equations for the dissolution in the inhomogeneous temperature field.

## The variational principle

The dynamics of a fluid can be divided into the kinetic part and thermodynamics part. The kinetic part of the dynamics for the fluid is characterized by the conservation laws for mass, energy, momentum, and angular momentum. On the other hand, the thermodynamics is described by the equation of the entropy in the form as

$$\frac{\partial}{\partial t}(\rho s) = \Theta - \nabla \cdot \mathbf{J}, \quad (1)$$

where  $\rho$  is total mass density,  $s$  is specific entropy,  $\mathbf{J}$  is entropy flux, and  $\Theta > 0$  is a dissipative function describing entropy production rate per time. The equation (1) plays an important role in connecting the kinematics and thermodynamics. In terms of the variational principle, we define the Lagrangian density as the kinetic energy density minus the internal energy density, and the action as the integral over space and time. The realized dynamics minimizes the action under some constraints[5, 6, 7, 8, 9, 10]. With the aid of (1), this principle enables us to formulate the dynamics of the fluid even if it has complicated con-

straints. Noether's theorem states that each of the conservation laws is associated with each corresponding symmetry. For example, the conservation laws for energy, momentum, and angular momentum are related to the translation symmetries in time and space, and rotational symmetry, respectively. Thus to satisfy these conservation laws, (1) has to be consistent with these symmetries. If we don't know the exact form of the dissipative function  $\Theta > 0$ , we can fix it by considering the symmetries. On the other hand, the entropy flux  $\mathbf{J}$  is determined to erase surface terms without fixing boundary conditions appearing in the variational calculus. Our method is very simple. We just give the Lagrangian by the kinetic energy minus the internal energy. The exact form of (1) is obtained by the method above.

## The two-component fluid

We consider a two-component fluid composed of two substances: solute and solvent. The conservation law of the total mass  $\rho$  is given by

$$\frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (2)$$

where  $\mathbf{v}$  is mass average velocity. We introduce the set of three scalars  $\mathbf{A} = (A_1, A_2, A_3)$  denoting the initial position of the fluid particle at  $(t, \mathbf{x})$ . By the definition, the material derivative  $D_t \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$  of  $A_i$  is zero,

$$D_t A_i = 0. \quad (3)$$

In the variational calculus, we use  $\mathbf{A}$  to describe the path lines of the fluid particles, and fix the value of  $\mathbf{A}$  at the boundary. Let  $\psi$  be the mass fraction of the solute. The mass conservation law of the solute is

$$\rho D_t \psi + \nabla \cdot \mathbf{j} = 0, \quad (4)$$

where  $\mathbf{j}$  is the diffusion flux of the solute. The diffusion flux  $\mathbf{j}$  describes the relative motion of the solute and the solvent. Let  $\mathbf{a}$  be the amount of the solute flowing through the unit interface orthogonal to the direction of  $\mathbf{j}$ , i.e.,

$$D_t \mathbf{a} - \mathbf{j} = 0. \quad (5)$$

We also fix the value of  $\mathbf{a}$  at the boundary. The main purpose is to obtain the equations for  $\mathbf{v}$  and  $\mathbf{j}$  from the variational principle. We define the specific bulk

internal energy  $\epsilon$  as the function of  $\rho$ ,  $\psi$ , and  $s$ . Here,  $s$  is the specific entropy of the two-component fluid. Thus we have

$$d\epsilon = -P d\rho^{-1} + \mu d\psi + T ds, \quad (6)$$

in the thermodynamics. Pressure  $P$  and temperature  $T$  are defined as  $P \equiv \rho^2 (\partial\epsilon/\partial\rho)_{s,\psi}$  and  $T \equiv (\partial\epsilon/\partial s)_{\rho,\psi}$ , where the subscripts  $s$ ,  $\rho$  and  $\psi$  indicate variables fixed in the respective partial differentiations. The coefficient  $\mu \equiv (\partial\epsilon/\partial\psi)_{s,\psi}$  is an appropriately defined chemical potential of mixture,  $\mu = \mu_{\text{solute}}/\mu_{\text{solute}} - \mu_{\text{solvent}}/\mu_{\text{solvent}}$ , where  $\mu_{\text{solute}}$  and  $\mu_{\text{solvent}}$  are the chemical potentials of the two substances, and  $m_{\text{solute}}$  and  $m_{\text{solvent}}$  are the masses of the two kinds of the particles as in §58 of Ref. [11]. We write  $E$  for the interface energy density given as the function of  $\rho$ ,  $\psi$ , and  $\nabla\psi$ , and assume that  $E$  is isotropic, i.e.,

$$\frac{\partial E}{\partial \partial_i \psi} \partial_j \psi = \frac{\partial E}{\partial \partial_j \psi} \partial_i \psi. \quad (7)$$

The internal energy density is the sum of the bulk energy density and the interface energy density,

$$\rho\epsilon + E. \quad (8)$$

On the other hand, the total kinetic energy density is the sum of the kinetic energy densities of the each fluid, and it is rewritten into

$$\frac{1}{2}\rho \mathbf{v}^2 + \frac{1}{2\rho} \left( \frac{1}{\psi} + \frac{1}{1-\psi} \right) \mathbf{j}^2. \quad (9)$$

The Lagrangian density  $\mathcal{L}$  is given by subtracting (8) from (9),

$$\mathcal{L} \equiv \rho \frac{1}{2} \mathbf{v}^2 + \frac{1}{2\rho} \left( \frac{1}{\psi} + \frac{1}{1-\psi} \right) \mathbf{j}^2 - (\rho\epsilon + E). \quad (10)$$

Next, let us discuss the thermodynamics. Considering the translation symmetries in time and space, which are respectively associated with the conservation laws of energy and momentum, the equation of the entropy (1) is given in the form of

$$\rho D_t s = \frac{(\sigma_{ij} \partial_i \nu_j - \nabla \cdot \mathbf{J}_q + \boldsymbol{\nu} \cdot D_t \mathbf{a})}{T} - \nabla \cdot \mathbf{J}_s. \quad (11)$$

Here  $\sigma$  and  $\boldsymbol{\nu}$  are coefficients, and  $\mathbf{J}_q$  is heat flux. Note that  $\nu_j$  is the function of  $\partial A_i / \partial t$  and  $\partial_j A_i$  from (3). We determine  $\mathbf{J}_s$  as

$$\mathbf{J}_s = \frac{1}{T} \frac{\partial E}{\partial \nabla \psi} D_t \psi \quad (12)$$

to erase the surface term with respect to  $\psi$  appearing in the variational calculus of the Lagrangian (10). Here  $\partial E/\partial \nabla \psi$  takes large absolute value at the interface, and  $D_t \psi$  expresses the moving of the interface. Thus (12) shows that entropy flux occurs with accompanying the moving interface, which is related to the heat of dissolution[12]. The coefficient  $\sigma$  is a symmetric tensor because of the rotational symmetry corresponding to the conservation law of angular momentum. We can rewrite (11) in the form of (1). Then  $\Theta$  and  $\mathbf{J}$  are respectively given by

$$\Theta = \frac{1}{T} (\sigma_{ij} e_{ij} + \boldsymbol{\nu} \cdot \mathbf{j}) + \mathbf{J}_q \cdot \nabla \left( \frac{1}{T} \right), \quad (13)$$

$$\mathbf{J} = \rho s \mathbf{v} + \frac{\mathbf{J}_q}{T} + \mathbf{J}_s. \quad (14)$$

Here  $e_{ij} \equiv (\partial_i v_j + \partial_j v_i)/2$  is the strain rate tensor. We determine  $\sigma$ ,  $\boldsymbol{\nu}$ , and  $\nabla T$  to make (13) positive because of the second law of thermodynamics. In the low degree approximation, (13) is given by the quadratic form of  $e_{ij}$ ,  $\mathbf{j}$ , and  $\nabla T$ . If we assume that  $\sigma_{ij}$  depends on only  $e_{ij}$  and is isotropic, we have

$$\sigma_{ij} = 2ae_{ij} + (b - 2a/3)\delta_{ij}e_{kk}, \quad (15)$$

where  $a$  and  $b$  are the coefficients of shear and bulk viscosities, respectively. If the both of  $a$  and  $b$  are positive,  $\sigma_{ij}e_{ij}$  is also positive. Without loss of generality, we have

$$\boldsymbol{\nu} = \xi \mathbf{j} + \eta \nabla T, \quad (16)$$

$$\mathbf{J}_q = -\eta T \mathbf{j} - \kappa \nabla T, \quad (17)$$

where  $\xi$  is the coefficient of friction for the diffusion flux  $\mathbf{j}$ , and  $\kappa$  is the coefficient of thermal conductivity. The coefficient  $\eta$  in (16) expresses the Soret effect describing the flow of the solute induced by a temperature gradient. On the other hand, the coefficient  $\eta$  in (17) shows the Dufour effect describing the energy flux due to the diffusion flux  $\mathbf{j}$  occurring. The both of  $\eta$  in (16) and (17) expresses coupled effects of irreversible processes. The coefficients  $\xi$ ,  $\eta$ , and  $\kappa$  are determined to make (13) positive[3].

The action is given by the integral of (10) over the considered time and space. By solving the stationary condition of the action subject to (2), (3), (4), (5), and (11), we obtain the equations of motion for the mass average velocity  $\mathbf{v}$ , and the diffusion flux  $\mathbf{j}$ . The former is

$$\frac{\partial}{\partial t} (\rho v_i) + \partial_j (\rho v_i v_j + \Pi_{ij} + \sigma_{ij}) = 0, \quad (18)$$

where we use (7), and write  $\Pi_{ij}$  for

$$\Pi_{ij} = \left( P + \rho \frac{\partial E}{\partial \rho} - E \right) \delta_{ij} + \frac{\partial E}{\partial \partial_i \psi} \partial_j \psi. \quad (19)$$

The latter is

$$D_t \left\{ \frac{1}{\rho} \left( \frac{1}{\psi} + \frac{1}{1-\psi} \right) \mathbf{j} \right\} = -\nabla \left\{ \mu^* + \frac{1}{2\rho^2} \left( \frac{1}{\psi^2} - \frac{1}{(1-\psi)^2} \right) \mathbf{j}^2 \right\} - \boldsymbol{\nu}, \quad (20)$$

where  $\mu^*$  is the generalized chemical potential defined as

$$\mu^* \equiv \mu + \frac{1}{\rho} \frac{\partial E}{\partial \psi} - \frac{T}{\rho} \partial_k \left( \frac{1}{T} \frac{\partial E}{\partial \partial_k \psi} \right). \quad (21)$$

If the diffusion flux  $\mathbf{j}$  is static and small, we have

$$\mathbf{j} = -\frac{1}{\xi} \nabla \mu^* - \frac{\eta}{\xi} \nabla T, \quad (22)$$

from (16) and (20). The equation (22) shows that the diffusion flux  $\mathbf{j}$  occurs in response to the gradients of the generalized chemical potential  $\mu^*$  and the temperature  $T$ . The third term in the right-hand side in (21) shows that the interface energy prevents the dissolution of the solute, when the temperature  $T$  is low.

## Summary and Discussion

We propose a new theoretical method based on the variational principle for the two-component fluid in inhomogeneous temperature field. In this proposed method, we combine the kinematics and thermodynamics by using (1) in the variational calculus. In this way, we obtain all the equations describing the whole dynamics of the two-component fluid. We clarify that the interface energy plays the important role in thermodynamics and dissolution as shown in (12) and (21), respectively. Previous theories based on a free energy[1, 2] assume a constant temperature and no heat flux in these theories, and cannot derive the entropy flux (12) and the generalized chemical potential (21). Our proposed method can be applied to various more complicated fluids, and yields the governing equations consistent with the conservation laws and thermodynamics[13]. What are required in our theory are the kinetic and the internal energy densities. The exact form of (1) is determined to satisfy symmetries

and the second law of thermodynamics, and to erase surface terms without fixing boundary conditions appearing in the variational calculus. The equations of motion are derived from the variational principle with the aid of (1).

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